

# PATENT SPECIFICATION

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## (54) CONTROLLED SUDS DETERGENT COMPOSITION

- (71) We, THE PROCTER & GAMBLE COMPANY, a Corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

may cause damage to the machine, and may cause the user to reduce the amount of detergent to a point where it is insufficient to yield the desired cleaning effect.

The suds profile of aqueous detergent solutions varies according to the temperature and water hardness of the particular aqueous solutions, the type and concentration of the detergent.

## ERRATUM

SPECIFICATION No. 1,304,803

Page 12, after line 114 insert new paragraph 14. A composition as claimed in Claim 10, wherein there is present from 0.1% to 1% by weight of silanated silica having a median particle size of from 10 mμ to 1 μ and a specific surface area above 50 m<sup>2</sup>/g.

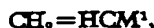
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 soluble organic builder, a suds controlling silicon containing agent, a copolymer of maleic anhydride and a vinyl compound and the water-soluble salts thereof, and optionally an inorganic hydrogen-peroxide addition compound as bleaching agent.  
 In many industrial and home operations involving aqueous solutions, the formation of suds is regarded as highly objectionable. Most prior art detergent compositions are high sudsing products; used in washing machines and laundering automatics they foam profusely, causing the machines or automatics to overflow with dense suds. In horizontal tumbler type washing machines, abundant suds decrease the washing action by interfering with the free fall of the laundry. Overflow of suds may cause damage to the machine, and may cause the user to reduce the amount of detergent to a point where it is insufficient to yield the desired cleaning effect.  
 The suds profile of aqueous detergent solutions varies according to the temperature and water hardness of the particular aqueous solutions, the type and concentration of the detergent.  
 cannot always be used because of their interaction with washing additives; while other interact with the soil, or are ineffective in highly alkaline solutions. All the said drawbacks restrict the use of the said suds controlled detergent compositions rather drastically.  
 It would be advantageous, therefore, to provide a detergent composition, in which sudsing can be controlled or even avoided at any use temperature, and particularly at high temperatures, i.e. from about 60° C to boiling temperature of the aqueous detergent solution, independent of its water hardness, its alkalinity, the intensity of agitation, without adversely influencing the whiteness maintenance properties of the detergent composition.  
 It is therefore, an object of this invention to provide a detergent composition, the sudsing

SEE ERRATA SLIP ATTACHED

of which can be substantially completely controlled at any usage temperature, and particularly at high temperatures, i.e. from about 60° C to boiling temperature, without adversely affecting its whiteness maintenance properties.

The present invention is based on the observation that the sudsing or foaming of a detergent composition, containing from 2% to 30% by weight a non-cationic organic surface active agent, and optionally a builder, usual detergent additives, and a bleaching agent, can be completely controlled without affecting the whiteness maintenance properties, by incorporating, calculated by weight on a finished product basis: (A) from about 0.05% to about 5% by weight, of a suds controlling agent chosen from the group consisting of silicones; finely divided silanated silica; particulated hydrophobic polymers and copolymers of styrene, ethene, fluoroethene, butene and isobutene, and mixtures thereof; and (B) from about 0.5% to about 8% by weight, of a polymeric compound selected from polymers of a vinyl compound having the formula



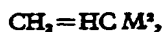
wherein  $M^1$  represents a pyrrolidone ( $\text{C}_4\text{H}_7\text{ON}$ ) radical, a  $-\text{OCOCH}_3$ ,



30  $-\text{OCH}_3$ ,  $-\text{OC}_2\text{H}_5$  radical, and copolymers thereof, having a molecular weight from 5,000 to 50,000; polymers of the general formula



35 having a molecular weight from 1,000 to 50,000; copolymers of maleic acid anhydride and a vinyl compound of the formula



40 wherein  $M^2$  represents a  $\text{C}_{1-4}$  alkyl ether radical, preferably a methyl ether radical, a phenyl radical, or a hydrogen atom, and the water-soluble salts thereof, having a molecular weight from 10,000 to 300,000.

Preferred detergent compositions contain, calculated by weight on a finished product basis: (a) from about 2% to about 30% of a water-soluble, organic, synthetic non-cationic surface active agent, preferably from 7% to 14% of a sulphuric acid reaction product; (b) from about 15% to about 80% of a water-soluble builder, preferably from 15 to 45% of an inorganic builder, used alone or in combination with a water-soluble organic builder, (c) from about 0.05% to about 3% of a suds-controlling agent selected from silicones, silanated silica, and preferably mixtures of both; (d) from about 0.5% to about 5%, preferably 1.0% to 2.5% of a maleic anhydride/

vinyl  $\text{C}_{1-4}$  alkyl ether copolymer, preferably maleic anhydride/vinyl methyl ether copolymer, and the water-soluble alkali metal salts thereof; and (e) optionally from about 12% to about 50% of a hydrogen peroxide addition compound, preferably from 25% to 35% of sodium perborate.

The compositions of this invention comprise the following compounds:

#### 1. Non-cationic surface active agents

(a) natural soaps. The soaps useful in the present invention are the ammonium and  $\text{C}_{1-3}$  alkanol ammonium (e.g. triethanol-ammonium) salts and preferably sodium and potassium salts of higher  $\text{C}_{8-18}$  fatty acids of naturally occurring plant or animal esters, e.g. palm oil, coconut oil, tallow, fish oils, lard and mixtures thereof.

(b) anionic synthetic non-soap detergents: a preferred class, can be broadly described as the water-soluble salts, particularly the alkali metal salts of organic sulfuric reaction products having, in their molecular structure, an alkyl radical containing from 8 to 22 carbon atoms and a sulfonic acid or sulfuric acid ester radical, (included in the term alkyl is the alkyl portion of higher acyl radicals). Preferred are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ( $\text{C}_{8-18}$  carbon atoms) and sodium or potassium  $\text{C}_{8-18}$  alkyl benzene sulfonates; sodium alkyl glyceryl ether sulfonates; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates, sodium or potassium salts of sulphuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulphate with 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids esterified with isothionic acid and neutralized with sodium hydroxide, and others known in the art.

(c) Nonionic synthetic detergents: broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl-aromatic in nature. Preferred classes of nonionic synthetic detergents are as follows:

(i) compounds formed by condensing ethylene oxide with a hydrophobic base, formed by the condensation of propylene oxide with propylene glycol, whereby said hydrophobic portions of the molecule has a molecular weight of from about 1500 to 1800, while the polyoxyethylene content is about 50% of the total weight of the condensation product.

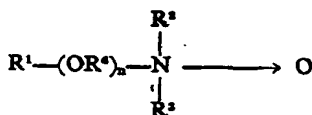
(ii) The polyethylene oxide condensates of  $C_{8-18}$  alkyl phenols with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol.

(iii) Nonionic synthetic detergents derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. For example, compounds containing from 40% to 80% by weight of polyoxyethylene, and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide; said bases having a molecular weight of the order of 2,500 to 3,000 are satisfactory.

(iv) The condensation product of aliphatic alcohols having from 8 to 22 carbon atoms with ethylene oxide, e.g. a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(v) The ammonia, monoethanol and diethanol amides of fatty acids having an acyl moiety of from about 8 to about 18 carbon atoms.

(vi) Long chain tertiary amines oxides corresponding to the following general formula

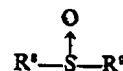


wherein  $R^1$  is an alkyl radical of from about 8 to about 24 carbon atoms,  $R^2$  and  $R^3$  are each methyl, ethyl, or hydroxyethyl radicals,  $R^4$  is ethylene, and  $n$  is 0 or an integer of up to 10. The arrow in the formula is a conventional representation of a semi-polar bond. Specific examples of amine oxide detergents include: dimethyl dodecyl amine oxide; acetyl dimethyl amine oxide; bis-(2-hydroxyethyl) dodecyl amine oxide; bis-(2-hydroxyethyl) - 3 - dodecoxy - 1-hydroxypropyl amine oxide.

(vii) Long chain tertiary phosphine oxides corresponding to the following general formula  $R^4R^5R^6P \longrightarrow O$  wherein  $R^4$  is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 24 carbon atoms in chain length and  $R^5$  and  $R^6$  are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond.

Examples of suitable phosphine oxides are found in British patent specification No. 95,260, and include: dimethyl dodecyl phosphine oxide; diethyl dodecyl phosphine oxide; and dimethyl 2-hydroxydodecyl phosphine oxide.

(v) Long chain sulfoxides having the formula



wherein  $R^7$  is an alkyl radical containing from 10 to 28 carbon atoms, from 0 to 5 ether linkages and from 0 to 2 hydroxyl substituents, at least one moiety of  $R^8$  being an alkyl radical containing no ether linkages and containing from 10 to 18 carbon atoms, and wherein  $R^8$  is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups. Specific examples of these sulfoxides are: 3 - methoxy tridecyl methyl sulfoxide; 3 - hydroxy - 4 - dodecoxybutyl methyl sulfoxide.

(d) Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic secondary and tertiary amines, wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g. carboxy, sulfo, sulfato, phosphato or phosphono. Examples of compounds falling within this definition are sodium 3 - dodecylaminopropionate and sodium 3 - dodecylamino - propane sulfonate.

(e) Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulphonium compounds, wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g. carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are 3 - (N,N - dimethyl - N - hexadecylammonio) propane - 1 - sulfonate and 3 - (N,N - dimethyl - N - hexadecylammonio) - 2 - hydroxy - propane - 1 - sulfonate which are specially preferred for their excellent cool water detergent characteristics. See, for example, British Patent 987,795.

## 2. Detergent Builders

The detergent builders useful in the present invention are water-soluble inorganic alkaline builder salts and organic alkaline sequestering builder salts and mixtures thereof as described and illustrated below.

Examples of water soluble inorganic alkaline builder salts (and mixtures thereof) which can be used in the compositions of this invention include the sodium, potassium, ammonium

and substituted ammonium carbonates, borates, phosphates, condensed polyphosphates, bicarbonates, and silicates. Specific examples of such salts are the sodium and potassium tri-  
 5 polyphosphates, carbonates, tetraborates, pyrophosphates, orthophosphates, bicarbonates and hexametaphosphates.

Examples of organic alkaline builder salts (and mixtures thereof) which can be used are  
 10 the alkali metal, ammonium or substituted ammonium aminopolycarboxylates; for example, sodium and potassium N - (s-hydroxyethyl) - ethylenediaminetriacetates and sodium and potassium nitrilotriacetates. Other  
 15 valuable polycarboxylate builders are the sodium and potassium salts of polymaleic, polyitaconic- and polyacrylic acids. The alkali metal salts of phytic acid are also suitable builders.

The polyphosphonates which can be used as builders for the compositions of this invention include compounds exemplified by the follow-  
 20 ing: sodium and potassium salts of ethene-1-hydroxy-1, 1-diphosphonic acid, sodium and potassium salts of methylene and ethylenedi-  
 25 phosphonic acids.

Additional examples of builders useful in the present invention are disclosed in the U.S. Patent 3,336,230.

3. Bleaching Agents—for example hydrogen peroxide addition compounds. The hydrogen peroxide addition compounds which can be incorporated into the composition of the present invention may be organic but are prefer-  
 35 ably inorganic in nature.

A great variety of these compounds exist. Most of them are prepared by crystallization from solutions containing  $H_2O_2$ . Others are prepared by drying a slurry containing the corresponding salts and  $H_2O_2$ . The most useful  
 40 hydrogen peroxide addition compounds are the perborates, e.g., the sodium perborate mono- and tetrahydrates. Other useful perborates are the potassium and ammonium perborates  
 45 having the formulae  $2KBO_3 \cdot H_2O$  and



respectively. Other valuable hydrogen peroxide addition compounds are the carbonate peroxyhydrates, e.g.,  $2Na_2CO_3 \cdot 3H_2O_2$ , and the  
 50 phosphate peroxyhydrates, e.g. sodium pyrophosphate peroxyhydrate  $Na_4P_2O_7 \cdot 2H_2O_2$ . The most suitable organic hydrogen peroxide addition compound which can be incorporated into the detergent composition of the present in-  
 55 vention is the urea hydrogen peroxide addition compound of the formula  $CO(NH_2)_2 \cdot H_2O_2$ , because it is one of the few free flowing dry organic hydrogen peroxide addition com-  
 60 pounds.

4. Suds controlling agent. The suds control-

ling agents which have proved useful according to the present invention are:

(a) silicones. In industrial practice, the term "silicone" has become a generic term covering all high molecular weight polymers containing siloxane units and organic groups, in which the siloxane unit  $-Si-O-$  constitutes the continuing backbone.

The silicones useful in the present invention are high molecular weight linear or cyclic polymers, in which the  $-Si-O-$  unit constitutes the continuing backbone, and in which the organic substituents are saturated and unsaturated  $C_{1-4}$  alkyl radicals, optionally substituted by a hydroxyl group, and are aryl radicals. Preferred are dimethyl and methylphenyl silicones also called polydimethyl- and polymethylphenyl siloxanes whereby the ratio of the molecular weight of the hydrocarbon radicals to the atomic weight of the silicon atoms varies within the range from 0.5/1 to 6/1, preferably from 1.8/1 to 2.2/1, having a viscosity from 5 to 500,000 centistokes, preferably from 200 to 25,000 centistokes at 25° C.

The silicones useful in this invention preferably contain other siliceous material such as finely particulated inorganic silica, for example, in the form of an siliceous aerogel. The addition of up to 20% by weight, e.g., from 3% to 10% by weight, calculated on the weight of silicones, of silica or silicon dioxide, is highly recommendable to obtain excellent suds controlling results near boiling temperatures, especially with dimethyl silicones. The particle size of the silica dioxide should be at most 25  $m\mu$ , preferably from 10 to 20  $m\mu$ , and the specific surface area above 50  $m^2/g$ .

(b) silicone-silica compounds. The silicone-silica compounds useful in the present invention consist of silicones to which finely divided inorganic silica or silicon dioxide is bound chemically including polymeric silicones in which the continuing backbone of siloxane units is interrupted by a silicon dioxide particle, an example of which is described in the U.S. Patent 3,388,073.

(c) silanted silica. Silanted silica useful in the present invention can be made by reacting a hydrophobic silica, produced by vapor-phase hydrolysis of silicon tetrachloride, with, for instance, dimethyl dichlorosilane, or by physically affixing the hydrophilic silica to a polysilicone as described in the U.S. Patent 3,207,698.

The silanted silica to be used in the present invention must have a median particle size of from 10  $m\mu$  to 1  $\mu$ , a purity above 85%, and a specific surface area above 50  $m^2/g$ . The preferred silanted silica has a median particle size from 10 to 50  $m\mu$ , a specific surface above 100  $m^2/g$ , while a 1% by wt. concentration of

the silanted silica in a 1:1 water-isopropyl alcohol mixture has a pH above 7. The amount of silanted silica in the detergent composition is preferably from 0.1% to 1.0% by weight.

Preferred siliceous suds controlling agents are 3/1 to 1/2 mixtures by weight of (1) silicones, preferably dimethyl and methylphenyl silicones, of which the ratio of the molecular weight of the hydrocarbon radicals to the atomic weight of the silicon atoms varies within the range from 1.8/1 to 2.2/1, having a viscosity of about 1,000 to 5,000 centistokes at 25° C and containing about 3% to 5% by weight of finely divided silica, and (2) silanted silica, preferably silanted silica having a median particle size of 10—25  $\mu$ , and a specific surface area above 200  $\text{m}^2/\text{g}$ . The preferred amount of mixtures of silicones and silanted silica in the detergent composition of the present invention should vary within the range from 0.05% to 0.5% by weight.

(d) particulated hydrophobic polymers and copolymers of styrene, ethene, fluoroethene, propene isobutene, having a median particle size of less than 100  $\mu$ , preferably less than 50  $\mu$ . The preferred amount of particulated hydrophobic polymers and copolymers incorporated into the detergent composition of the present invention should vary within the range from 1.5% to 3% by wt.

5. Polymeric compound. The polymeric compounds useful in the present invention are polymers of a vinyl compound having the formula  $\text{CH}_2=\text{CHM}^1$ , wherein  $\text{M}^1$  represents a pyrrolidone ( $\text{C}_4\text{H}_6\text{ON}$ ) radical, a



$-\text{OCOC}_2\text{H}_5$ ,  $-\text{OCH}_3$  or  $-\text{OC}_2\text{H}_5$  radical, and copolymers thereof, having a molecular weight within the range from 5,000 to 50,000; polymers having the general formula



having a molecular weight within the range from 1,000 to 50,000; copolymers of maleic anhydride and a vinyl compound of the formula  $\text{CH}_2=\text{CHM}^2$ , wherein  $\text{M}^2$  represents a  $\text{C}_{1-4}$  alkyl ether radical, or a H-atom, and the water-soluble salts thereof, having a molecular weight within the range from 10,000 to 300,000. The salts can be alkali metal or ammonium or substituted ammonium salts, preferably the sodium and potassium salts. The salt can be used in a partially or fully neutralized form.

A finished detergent composition of this invention will contain minor amounts of materials which make the product more attractive. The following are mentioned by way of

example: a tarnish inhibitor such as benzotriazole or ethylene thio-urea can be added in amounts up to 2% by weight; fluorescers, perfumes and dyes, while not essential, can be added in small amounts. Sodium carboxymethyl cellulose may be added in small amounts to inhibit soil redeposition; an alkaline material such as sodium or potassium carbonates or hydroxides can be added in minor amounts as supplementary pH adjusters. There may also be mentioned, as suitable additives: bacteriostats, bactericides, enzymes, corrosion inhibitors such as soluble alkali silicates, preferably sodium silicates having an  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of from 1:1 to 2.8:1, and textile softening agents.

These ingredients of the compositions of this invention are generally employed in the form complete detergent formulations. These complete detergent formulations can be prepared in any of several forms, including granular, powdered, flake or tablet, and in any suitable manner as long as they contain the amounts of surface active non-cationic agent, suds depressant and polymeric compound set forth herein. Numerous methods are known in the art for preparing said compositions; for instance, each of the ingredients can be admixed according to the stated amounts, or some of the ingredients can be slurried and spray-dried, whereafter the more heat-sensitive ingredients as for example the hydrogen peroxide addition compounds and the perfume, are mixed with the spray-dried ingredients, or the ingredients can be agglomerated as described in the British Patent 990,252.

The effectiveness of the detergent compositions of this invention is illustrated by the following tests. All compositions were prepared by mixing the surface active agent, fatty acid, builder salt, electrolyte and CMC in a crutcher, spray-drying the crutcher mix, and admixing the silicone, copolymer and perborate.

The laundry screening test to which reference is made in the "Tests" following hereinafter, is a test method which was developed to determine the suds profile of any low sudsing detergent formulation. These tests are conducted in a smaller than normal, specially designed, horizontally rotating drum washing machine, which simulates as closely as possible the agitation, temperature control, detergent concentration, and water conditions of an actual tumbler type washing machine in operation. The machine is so designed (with a transparent front), that the suds height and water temperatures can be visually observed, easily measured, and recorded throughout any specific test. In this way, the actual sudsing, if any, in response to the load, detergent concentration, soil, water hardness and increase in temperature can be observed.

## TEST A

Four series of different detergent compositions were prepared consisting of

ingredients (in % by wt.)	A	B	C	D
— stearyl dimethyl amine oxide	10	10	10	10
— tallow alcohol-ethylene oxide condensate (oxide units : 11)	2	2	2	2
— hydrogenated fatty acids (average mol. weight : about 285)	3	3	3	3
— sodium tripolyphosphate	32	32	32	32
— sodium perborate tetrahydrate	32	32	32	32
— sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=2.1$ )	6.3	6.3	6.3	6.3
— sodium sulphate	6.2	6.2	6.2	6.2
— carboxymethyl cellulose (CMC)	1	1	1	1
— silicone <sup>1</sup> (dimethyl silicone compounded with 3% silica; viscosity at 25°C : about 3000 cts.)	—	0.22	0.22	0.44
— Na salt of maleic anhydride/vinyl methyl ether copolymer (molecular weight of copolymer in anhydride form : 250,000; ratio of monomers 1:1)	—	—	1	1
— water	balance			

Four series of five aqueous solutions were prepared, each series containing 1% by weight of one of the compositions A, B, C and D. The water used was tap water having a water hardness of 3.5 milli-moles of  $\text{CaCO}_3$  per litre.

The screening test washing machines were loaded with cotton swatches (liquid/fabric load weight ratio: 8/1), and 0.025% by weight, calculated on the aqueous washing solution, of a mixture of oleic acid, olein, and light mineral oil (ratio 1:1:1) was added under agitation.

The cotton swatches were washed during 50 minutes under agitation (the rotator spinning at about 50 rpm throughout the entire washing cycle); during which time the water temperature was raised from room temperature to boiling.

At the end of the heat-up cycles, the cotton swatches were squeezed, rinsed twice by hand in tap water (hardness 3.5 millimoles

$\text{CaCO}_3/1$ ),

submitted to a spin (10 minutes) and dried in an air dryer (20 minutes).

The washed cotton swatches were then again soiled, washed, rinsed and dried under the same circumstances as described above, and consequently submitted to a third series of identical soiling, washing, rinsing, and drying operations.

The suds heights of the three washing cycles of the five solutions of the four series were recorded at 40° C and at boiling temperature,

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Average suds heights in cm	A	B	C	D
at 40°C.	15	7	7	5
at boiling temperature	25	10	10	8

The three times washed swatches were then inspected with a Hunter D25 Colour Difference meter with inserted ultra-violet screens, for whiteness (Hunter Ass. Laboratory Inc. Virginia, U.S.A.) The whiteness effects are

expressed as Hunter L—values, whereby the least significant difference at 95% confidence limit (LSD=0.95) is 1 L. The average whiteness L-values of the cotton swatches washed in the five solutions were:

A	B	C	D
75	74	78	77.4

From said tests it can be seen that the aqueous solutions containing 1% of composition A suds excessively, especially at high temperature, and that the swatches washed in solutions containing 1% of composition B show a poorer whiteness L-value than those washed in solutions containing the same concentration of A, C, and D, while the aqueous solutions containing 1% by weight of composition C or D are superior to both A and B in depressed suds profile and whiteness L-values.

#### TEST B

The four series of tests, described in Test A, were repeated in a tumbler type washing machine in general use throughout Western Europe, under the following conditions: only two aqueous solutions of each composition were prepared; the cotton swatches and artificial soil were replaced by naturally soiled T-shirts, nylon shirts, towels and polyester/cotton sheets. Said bundle of family laundry was introduced into the washing machine, soaked for 12 minutes in tap water (hardness: 3.2 millimoles  $\text{CaCO}_3/\text{l}$ ; temperature: 18° C; load: 3.5 kg in 28 l); washed during 45 minutes in fresh tap water (about 33 l) containing 1% by wt. of composition A, B, C,

and D respectively, whereby the temperature was raised from 18° C to 92° C; and rinsed twice with about 28 l of fresh tap water, and dried.

The aqueous solution containing 1% by weight of composition A oversuds during the washing cycle at a temperature of about 40° C; the cleaning of the different items washed in said solution was poor and unacceptable.

The items washed in the solutions containing 1% by weight of the compositions B, C, and D respectively, were again soiled and washed twice, and the whiteness L-values compared after having been washed in a third washing cycle. The difference in whiteness L-values was the same as mentioned above for the cotton swatches washed with compositions B, C, and D. (Test A).

#### TEST C

When the stearyl dimethyl amine oxide of the compositions A, B, C, and D were replaced by the same percentage of sodium alkylbenzene sulphonate (average C-atoms in the alkyl radical: 11.8), and the same screening tests were carried out with cotton swatches and artificial soil as described hereinbefore (Test A), the following results were obtained:

suds heights (in cm)	E	F	G	H
at 40°C	10	0	70	0
at boiling-point	20	5	5	0
whiteness L-values	79.8	78	79.5	79.6
(after third washing cycle)				

#### TEST D

When the silicone in the compositions A, B, C, and D, and E, F, G, and H was replaced by a corresponding amount of a dimethylsilicone having a viscosity at 200,000 cts at 25° C, the average suds heights were approximately the same; and when replacing it by a corresponding amount of a 1:1 mixture of (a) a dimethylsilicone compounded with 3% by wt. of a silica having a viscosity of 3,000 cts at 25° C, and (b) a silanated silica with a medium particle size of about 15  $\mu$ , and a specific surface area of about 215  $\text{m}^2/\text{g}$ , the suds were reduced by about 50% (for B, C, and D) or disappeared substantially completely even at boiling temperature (for F and G), while in all tests the whiteness L-values were the same, as mentioned above for the corresponding compositions (Tests A and C).

#### TEST E

When replacing the 0.025% by weight of the soil consisting of oleic acid, olein and light

mineral oil, (Tests A) by the same amount of a mixture of 8 parts of soil taken from air condition filters (35% of inorganic material, mainly ash; 59% of different organic compounds, e.g. lipids; 6% moisture) and 2 parts of a blend of oleic acid, olein and light mineral oil (ratio 1:1:1), of which a slurry has been made by dispersing said mixture in tap water using a high speed agitator, and repeating the four series of five tests with cotton swatches as described for compositions A, B, C, and D above (Test A), the suds heights and difference in whiteness L-values were the same.

#### TEST F

Another series of five tests were carried out as described in Test A, but with the following compositions: (see Table I), of which the excellent foam suppression and whiteness maintenance is again apparent for compositions J, L, N, P, R, and T and V, formulated according to this invention.





TABLE I (Continued)

Ingredients (in % by wt.)	I	J	K	L	M	N	O	P	Q	R	S	T	U	V
— sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=2.0$ )	6	6	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3	6.3
— sodium sulphate	8.5	7.5	6.2	6.2	7.2	6.2	15.2	14.2	21	20	7.2	6.2	7.2	6.2
— carboxymethylcellulose	1	1	1	1	1	1	1	1	1	1	1	1	1	1
— silicone (see comp. A)	0.22	0.22	—	—	0.11	0.11	0.44	0.44	0.22	0.22	—	0.44	0.22	0.22
— silanated silica (median particle size : about 15 m $\mu$ , specific surface area : about 215 m <sup>2</sup> /g.)	—	—	0.22	0.22	0.11	0.11	—	—	—	—	—	—	—	—
— maleic anhydride/vinyl methyl ether copolymer (see (see composition A)	—	1	—	—	—	1	—	1	—	1	—	1	—	1
— vinylpyrrolidone/vinyl acrylate copolymer (Na salt) (molecular weight : about 25,000)	—	—	—	1	—	—	—	—	—	—	—	—	—	—
— water	balance													
suds heights (average of 15)														
— at 40°C	0	0	15	15	0	0	0	0	0	0	12	0	5	5
— at boiling point	5	5	0	0	2	2	0	0	6	0	30	5	10	9
whiteness L-values (after third washing cycle)	78.3	79.8	78.3	79.5	78.3	79.8	77.7	79.1	78	80	76	77.8	75	78

The following examples illustrate the invention, the percentages being by weight.

#### Example I

A free flowing, finely divided detergent composition was prepared by slurring, in a crutcher, the surface active agents, builders, electrolytes, carboxymethylcellulose, brightener and water; spray-drying the slurry; dry-mixing the sodium perborate, copolymer and suds controlling agent with the spray-dried granules, and atomizing the perfume onto the agglomerates. The end product consisted of:

9.30%	linear alkyl benzene sulphonate sodium salt (average molecular weight of alkyl benzene 241),
26.10%	sodium tripolyphosphate,
3.40%	hydrogenated fatty acid (average mol. weight 285),
3.40%	condensation product of tallow alcohol and 11 moles ethylene oxide per mole alcohol,
6.20%	sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=2.1$ ),
0.80%	carboxymethylcellulose,
0.40%	toluene sulphonate sodium salt,
1.50%	sodium salt of the maleic anhydride-vinyl methyl ether copolymer (mol. weight about 200,000, monomer ratio 1:1)
0.20%	dimethylsilicone (viscosity: 200,000 cts at 25° C),
13.00%	sodium sulphate,
25.00%	sodium perborate tetrahydrate,
2.10%	brightener, perfume,
8.60%	moisture.

35 An aqueous solution (tap water) containing 1% of said composition when used in a tumbler type washing machine or in a conventional top loading automatic washer, yielded only reduced suds at any temperature between room temperature and 92° C, and cleaned thoroughly.

40 Other compositions found to be suitable were the following:

#### Example II

9.00%	laurylphosphine oxide,
25.00%	sodium tripolyphosphate,
2.00%	sodium ethylene diaminetetraacetate,
1.08%	carboxymethylcellulose,
3.60%	sodium toluene sulphonate,
27.00%	sodium sulphate,
17.50%	sodium perborate-tetrahydrate,
2.00%	sodium chloride,
1.40%	styrene-maleic anhydride copolymer (monomer ratio 1:1; molecular weight: about 50,000),
0.45%	silanated silica (median particle size: about 20 $\mu$ ; specific surface area: about 180 $\text{m}^2/\text{g}$ );

1.00%	enzyme product (40% active protease),
2.55%	miscellaneous,
7.50%	moisture.

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The copolymer may be replaced by the sodium salt of a maleic anhydride-ethylene copolymer (mol. wt. 150,000) or by the ethanolamide derivative of the maleic anhydride-vinyl ethyl ether copolymer (mol. wt.: 25,000).

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#### Example III

27.00%	sodium coconut alcohol sulphate,
25.00%	sodium tripolyphosphate,
4.00%	sodium nitrilotriacetate,
21.00%	sodium sulphate,
1.50%	enzyme products (40% active enzyme mixture containing 8 parts of protease and 2 parts of amylase);
3.60%	sodium toluene sulphonate,
4.00%	sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=1.6/1$ ),
2.50%	Sodium salt of maleic anhydride-vinyl methyl ether copolymer (monomer ratio: 2:1; molecular wt.: 75,000),
0.80%	methyl-phenyl silicone, compounded with 2.5% by wt. of silica (viscosity at 25° C: about 150,000 cts),
2.60%	miscellaneous (perfume, brightener, dyes),
8.00%	moisture.

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75

80

85

#### Example IV

7.00%	sodium 3 - (N,N - dimethyl - N-tetradecylammonio) - propane - 1-phosphate,
40.00%	sodium tripolyphosphate,
27.50%	sodium perborate tetrahydrate,
9.50%	sodium sulphate,
4.50%	sodium salt of maleic anhydride-vinyl methyl ether copolymer (monomer ratio 1:1; mol. wt. 50,000),
0.30%	silanated silica (particle size: 15 $\mu$ , specific surface area: 215 $\text{m}^2/\text{g}$ ),
9.70%	sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=1.6/1$ )
balance:	moisture, perfume

90

95

100

#### Example V

17.30%	sodium linear alkyl benzene sulphonate (C: 11.9),
40.50%	sodium tripolyphosphate,
4.00%	sodium nitrilotriacetate,
2.00%	sodium ethylene - 1 - hydroxy - 1,1-disphosphonate,
0.50%	monoethanolamine,
0.50%	methyl - phenyl silicone (viscosity 200,000 cts at 25° C),
2.50%	sodium salt of maleic anhydride-vinylmethyl - ether copolymer (monomer ratio 2:3; mol. wt. 225,000),

105

110

115

- 6.00% sodium silicate (SiO<sub>2</sub>/Na<sub>2</sub>O=1.6/1),  
2.00% sodium toluene sulphonate,  
12.00% sodium sulphate,  
5 3.20% miscellaneous (minor ingredients),  
9.50% moisture.
- Example VI
- 5.00% tallow alcohol - ethylene oxide (11)  
condensate,  
10 45.00% sodium tripolyphosphate,  
18.00% chlorinated trisodiumphosphate,  
20.00% sodium silicate (SiO<sub>2</sub>/Na<sub>2</sub>O=2.8/1),  
1.50% sodium salt of maleic anhydride-  
15 vinyl butyl ether copolymer (mono-  
mer ratio 1:1; mol. wt. 150,000),  
2.00% sodium salt of vinylpyrrolidone-vinyl  
2 acetate copolymer (monomer ratio  
1:1; mol. wt. 50,000),  
20 0.50% of a 1:1 mixture of dimethylsilicone  
(viscosity 200,000 ccs at 25° C) and  
silanated silica (median particle  
size: 15 mμ; specific surface area  
215 m<sup>2</sup>/g; pH in 1:1 mixture of  
25 water/isopropyl-alcohol: 8.59);  
8.00% moisture.
- WHAT WE CLAIM IS:—
1. A detergent composition comprising  
30 (a) from 2% to 30% by weight of a water-  
soluble, organic, non-cationic surface active  
agent;  
(b) from 0.05% to 5% by weight of a suds  
controlling agent selected from: silicones,  
35 finely divided silanated silica, finely divided  
hydrophobic homopolymers and copoly-  
mers of styrene, ethene, fluoroethene,  
butene and isobutene; and mixtures thereof;  
and  
40 (c) from 0.5% to 8% by weight of a homo-  
polymer of a vinyl compound having the  
formula CH<sub>2</sub>=HCM<sup>1</sup>, wherein M<sup>1</sup> repre-  
sents a pyrrolidone radical, a —OCOCH<sub>3</sub>,  
—OCOC<sub>2</sub>H<sub>5</sub>, —OCH<sub>3</sub>, —OC<sub>2</sub>H<sub>5</sub> radical,  
45 or a copolymer of more than one of these  
monomers, having a molecular weight from  
5,000 to 50,000; a polymer having a general  
formula —(CH<sub>2</sub>—CH<sub>2</sub>—O)— having a  
molecular weight from 1,000 to 50,000; or  
50 a copolymer of maleic acid anhydride and  
a vinyl compound of the formula  
CH<sub>2</sub>=HCM<sup>2</sup>, wherein M<sup>2</sup> represents a C<sub>1-4</sub>  
alkoxy radical, a phenyl radical, or a  
hydrogen atom, having a molecular weight  
55 from 10,000 to 300,000 or a water-soluble  
alkali-metal, ammonium or substituted  
ammonium salt thereof.
2. A composition as claimed in claim 1,  
wherein there is also present up to 80% by  
weight of a water-soluble builder salt.
- 60 3. A composition as claimed in claim 2,  
wherein the water-soluble builder salt is pre-  
sent in an amount from 15% to 45%.
4. A composition as claimed in any one of  
claims 1 to 3, wherein there is present 7% to  
14% by weight of water-soluble alkali-metal  
salt of an organic sulfuric reaction product  
having in its molecular structure an alkyl radi-  
cal containing from 8 to 22 carbon atoms and  
a sulfonic acid or sulfonic ester radical.
5. A composition as claimed in claim 1 or  
2 or in claim 4 is independent on claim 1 or  
2, wherein there is present from 15% to 80%  
by weight of a water-soluble inorganic builder  
salt, or mixtures thereof.
6. A composition as claimed in claim 5,  
wherein there is also present a water-soluble  
organic builder salt or a mixture of such salts.
7. A composition as claimed in any one of  
claims 2 and 3 to 6, when appendant to claim  
2, wherein there is present from 10% to 30%  
80 by weight of a water-soluble organic builder  
salt, or a mixture of such salts.
8. A composition as claimed in any one of  
claims 1 to 7, wherein there is present from  
12% to 50% by weight of a hydrogen peroxide  
addition compound.
9. A composition as claimed in claim 8,  
wherein there is present 25% to 35% of  
sodium perborate.
10. A composition as claimed in any one of  
claims 1 to 9, wherein there is present, as  
suds-controlling agent, 0.05% to 3% by weight  
of a silicone or a silanated silica or a mixture  
thereof.
11. A composition as claimed in claim 10,  
wherein the silicone present is a dimethyl-  
or methyl-phenyl silicone wherein the ratio of  
the molecular weight of the hydrocarbon radi-  
cals to the atomic weight of the silicon atoms  
varies from 0.5/1 to 6/1, and the said sili-  
100 cones have a viscosity from 5 to 500,000 centi-  
stokes at 25° C.
12. A composition as claimed in claim 11,  
wherein the ratio of the molecular weight of  
the hydrocarbon radicals to the atomic weight  
of the silicon atoms varies from 1.8/1 to 2.2/1  
and the silicones have a viscosity from 200 to  
25,000 centistokes at 25° C.
13. A composition as claimed in Claims 11  
or 12, wherein there is also present from 3%  
110 to 10% by weight, calculated on the weight of  
the silicones, of silicon dioxide having a  
median particle size of at most 25mμ, and a  
specific surface area above 50 m<sup>2</sup>/g.
15. A composition as claimed in any one of  
Claims 1 to 14 wherein component (c) com-  
prises from 0.5% to 5% by weight of a maleic  
anhydride-vinyl C<sub>1-4</sub> alkyl ether copolymer,  
and an alkali metal salt thereof, having a mole-  
120 cular weight from 10,000 to 300,000.
16. A composition as claimed in Claim 15,  
wherein component (c) comprises 1.0% to  
2.5% by weight of a maleic anhydride-vinyl  
methyl ether, and an alkali metal salt thereof,  
having a molecular weight from 75,000 to  
200,000.
17. A detergent composition as claimed in  
Claim 1 and substantially as described in any  
one of the Examples herein.

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